

Atmos. Chem. Phys. Discuss., referee comment RC3
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Comment on acp-2021-702

Anonymous Referee #3

Referee comment on "Ground-based investigation of HO_x and ozone chemistry in biomass burning plumes in rural Idaho" by Andrew J. Lindsay et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-702-RC3>, 2021

Review of Lindsay et al., "Ground-based Investigation of HO_x and Ozone Chemistry in Biomass Burning Plumes in Rural Idaho":

Summary: The authors measured total peroxy radical (XO₂) concentrations in McCall, Idaho, as part of a recent biomass burning intensive field campaign, with the goal of furthering our understanding of ozone and HO_x chemistry in biomass burning plumes. Five smoke plumes were sampled. The authors found that the ozone production rate, P(O₃), was not affected much by smoke plumes. Measured and modeled XO₂ concentrations were compared, showing reasonable agreement. The measurements are novel for biomass burning plumes, and the insights gained could be useful. However, I have major issues with the analysis used to justify whether or how much O₃ was enhanced in the measured plumes. The regular diurnal cycle of O₃ was not considered, and led to incorrect interpretations as detailed below. Major changes to that analysis would be needed prior to publication.

Major Comments:

Line 387 etc: I understand that the dO₃/dCO metric has been used before, but it seems to me that it is underconstrained here. Wouldn't the derived slope be strongly dependent on the time of day when the measurements were taken? O₃ has a strong diurnal cycle due to photochemistry, while CO does not. So across the several hours of measurements encompassing in-plume as well as pre/post plume background, the dCO term will likely be dominated by the addition of CO in vs out of the plume. However, the dO₃ term will be a sum of the O₃ added (or lost) from plume-specific chemistry plus any O₃ that would have been added (or lost) during the several hour measurement period due to regular photochemistry. With this in consideration, it appears that the slopes in Fig. S6 are most positive for the 22nd and 23rd because those data were taken during the early part of the

day when ambient O₃ concentrations were increasing most rapidly, while the slope for the 17th was smaller because the data came just shortly before peak daily O₃, and the slopes for the 24th and 16th (not shown) were smallest because the data came from after the daily peak of O₃ when mixing ratios were declining slowly. This might correlate with your calculated P(O_x), though it would depend on L(O_x) too I think. In other words, this method could work if it was using dO₃/dCO data that came from a short enough time span that the daily O₃ cycle was not a factor, for instance aircraft measurements spanning just a few minutes. But here, you're deriving a slope between in-plume data and out-of-plume data that are separated in time by several hours, during which time the actual O₃ in each air mass is changing (and changing in different ways depending on time of day of sampling). Therefore I do not think you can use this analysis to support your abstract-level conclusion that "During BB events, O₃ concentrations were enhanced..." at line 23. That conclusion may still be accurate, but you will need to provide better evidence.

Fig. 4: The same analysis as my previous comment applies here; O₃ has a prominent diurnal cycle that would exist with or without a wildfire plume, while HCN would not. Plume chemistry may enhance the O₃ cycle, but it apparently doesn't dominate it. Thus, the trends shown in this plot are driven by that underlying O₃ diurnal cycle. The slopes are steep and positive for data taken when a plume arrived during midmorning when O₃ is increasing due to ambient photochemistry, and shallow for data taken when a plume arrived after peak daily O₃. If you had a plume arrive at ~midnight, O₃ would be decreasing while HCN increased, giving a negative slope in Fig. 4. Therefore I do not think you are correctly interpreting the apparent positive correlation between O₃ and HCN here. The proper correlation would be between only the O₃ derived from smoke plume chemistry (i.e. subtracting the normal background photochemical diurnal cycle) vs. HCN. Obviously that's really difficult to parse and would likely require a model, so I'm not sure what to suggest other than removing this part of the analysis.

Line 354: Also, can you state here what is the R² value for the correlation in Fig. 4?

Line 376: I believe j(HONO) was measured, or could be estimated. Can you do a rough calculation of how much [HONO] would be needed to account for the added XO₂? That would be helpful for convincing the reader that it is reasonable to assume HONO is the missing factor.

Line 377: The fit line from Peng et al. 2020 (Fig. 3) suggests a value of more like 0.1 pptv/ppbv⁻¹ for average dHONO/dCO at 3 hours age, not 1 pptv/ppbv⁻¹ as stated here. However, the line is fit to all data regardless of in situ j_{HONO} , and some plumes did have elevated [HONO] at those ages, so it's possible this plume also did.

Line 404: Here you say "...there is little correlation between P(O_x) and smoke tracers." Then in the next sentences you discuss examples of how BB influences P(O_x). I would agree with the sentence at line 404. Also, Fig. 5a is not the correct plot to show to conclude that "P(O_x) is slightly higher during the afternoon and evening smoke influenced periods compared to non-smoke periods" as you say at line 408. I see the high [HCN] data covering a similar span of P(O_x) as low [HCN] data. Really to draw this conclusion

you would need to split the green trace (diurnal cycle of measured $P(O_x)$) into two, one with high HCN and one with low HCN to show the difference between them. Please do that, and then alter the text to tell a consistent story that there either is or is not a strong effect of smoke on $P(O_x)$ in your measurements.

Line 477: By plotting them together in Fig. 8, you're directly comparing measured $P(RO_x)$ from a subset of sources with modeled $P(RO_x)$ from all sources. They don't agree very well, nor should they agree, especially at night when alkenes+O₃ dominates. But this just adds confusion, and it doesn't help answer the real question of how well does the $P(RO_x)$ from measured sources compare with the $P(RO_x)$ modeled from the same subset of sources? I'd suggest maybe adding a dashed line for the $P(RO_x)$ modeled from that same subset for comparison, or altering the figure in some other way to help clarify so you're not comparing apples and oranges.

Minor Comments:

Line 33: add a citation here for Brazil and Australia fires

Line 272: It would be helpful if you refer to a specific location in the SI, e.g. Sect. S4 here. Please check other references to the SI as well.

Fig. 5: The figure panels are labeled $P(O_3)$, but should probably be $P(O_x)$ to be consistent with the caption and rest of text (and be consistent throughout).

Line 384: I'd prefer if you labeled the green and blue traces using a legend in the figure, rather than having to dig through the caption to find that information. Same goes for the $P(RO_x)$ speciation in the bottom panel of Fig. 3.

Line 418: Model Evaluation should be Sect. 3.3, not 3.2.